

Recent progress on innovative and potential technologies for glycerol transformation into fuel additives: A critical review

Norhasyimi Rahmat, Ahmad Zuhairi Abdullah^{*}, Abdul Rahman Mohamed

School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia

ARTICLE INFO

Article history:

Received 4 November 2009

Accepted 10 November 2009

Keywords:

Glycerol
Oxygenate fuel additive
Etherification
Acetylation
Acetalation
Catalyst

ABSTRACT

Glycerol emerges as a significant worth chemical that can be converted into high value products. In the prospect of biorefinery industries and great demand towards renewable sources, glycerol has proved to have tremendous potential to be transformed, thus supersede conventional petroleum derived fuel additive. Various types of oxygenated biocomponents and rigorous studies of glycerol transformation into fuel additives are presented in this review paper. Particular focus is given to etherification, acetylation and acetalation processes with specific behaviors in the respective reaction system.

© 2009 Elsevier Ltd. All rights reserved.

Contents

1. Introduction	987
2. Fuel additive	988
2.1. Oxygenate additive	988
3. Glycerol	989
4. Glycerol transformation into fuel additives	990
4.1. Physical properties	992
4.2. Reaction mechanism	992
4.3. Influence of catalyst	994
4.4. Influence of reactant	995
4.5. Influence of temperature	997
4.6. Influence of reaction time	997
5. Conclusion	998
Acknowledgements	998
References	998

1. Introduction

The development and commercial use of biodiesel has been encouragingly and rapidly expanding in Europe and US for over 10 years. The prominent superiority of biodiesel over petroleum diesel towards health and environment (free sulfur content, low content of harmful emission, e.g. particulate matter, HC, CO, etc.,

better lifecycle of CO₂ for global warming alleviation) as well as engine performance (enhance lubricity, high cetane number for complete combustion) [1,2] has enticed Asia to use biodiesel as alternative fuels and innovative solution to curb the polluted air emitted from growing vehicle population [3].

Despite the rapid pace of biodiesel development and commercialization, there are several key challenges emerging and these must be addressed efficiently. One key problem that is being ultimate focused is the inevitable low value production of glycerol as co-product of biodiesel from transesterification and esterification of vegetable oil [4]. Stoichiometrically, glycerol is produced by

^{*} Corresponding author. Tel.: +60 4 599 6411; fax: +60 4 594 1013.

E-mail address: chzuhairi@eng.usm.my (A.Z. Abdullah).

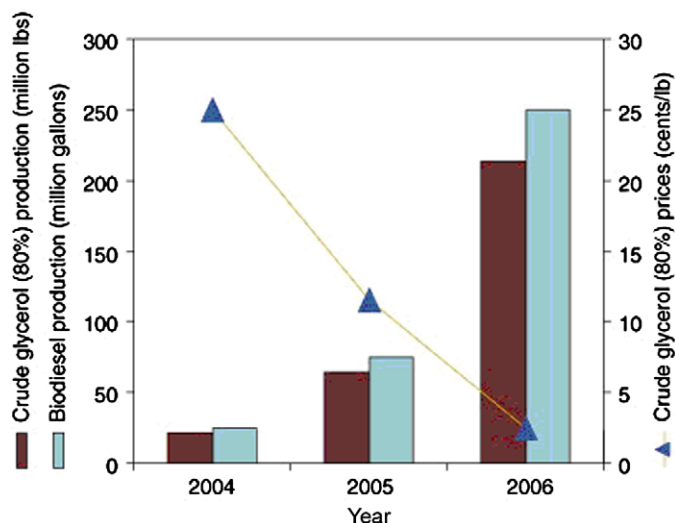


Fig. 1. Increasing production of biodiesel and crude glycerol lead to plummeting glycerol price [4].

10 wt.% of total biodiesel production. A sharp annual increase as high as 28% of biodiesel production in Europe from the year of 2000 has led to biodiesel production of 5 millions of metric tons (MTm) in 2006 [5] while in US, approximately 300 million gallons per year (gpy) of biodiesel is produced and expecting production increment of 600 million gpy in the next years [6]. The federal government Canada aimed to produce 500 million litres/year of biodiesel by the year 2010 to meet the Kyoto protocol [7], whereas in Malaysia, biodiesel production has been targeted to achieve 500,000 tone per year (tpy). The mass production of biodiesel would entail surplus glycerol production which has 80–88% purity [1]. The conventional application and current market of glycerol could not cope the excess production that need further costly purification step to meet the purity of crude glycerin of industrial grade (98% purity) [8]. A report from Tyson (2003) indicated that by taking into consideration the value of glycerol, the biodiesel cost production could be reduced from US\$ 0.63 L⁻¹ to US\$ 0.38 L⁻¹ [9]. Figs. 1–3 represent the biodiesel production over the years and its impact toward the price trend of glycerol. Major producers of glycerol like Malaysia and Indonesia, mostly derived from palm oils, seems to be the factor of glycerol price plummeting to US\$ 0.33 kg or below [9,10]. In US, Dow, Senenergy Chemical, ADM, Cargill and Ashland are all set to produce glycerol derived industrial products such as propylene and ethylene glycols which are adding to already

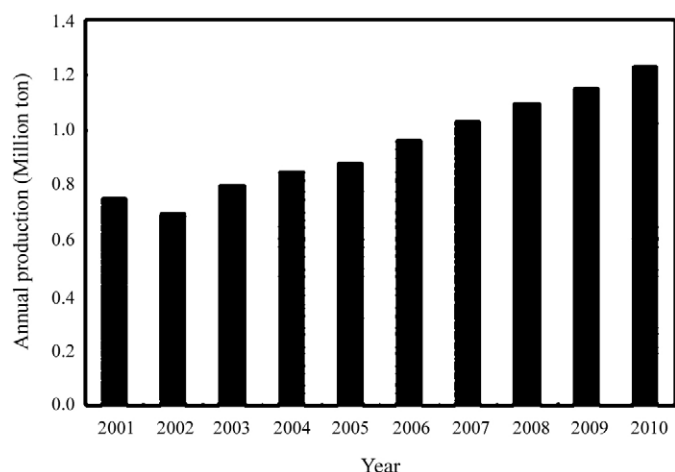


Fig. 2. Projection of the global glycerol production [4].

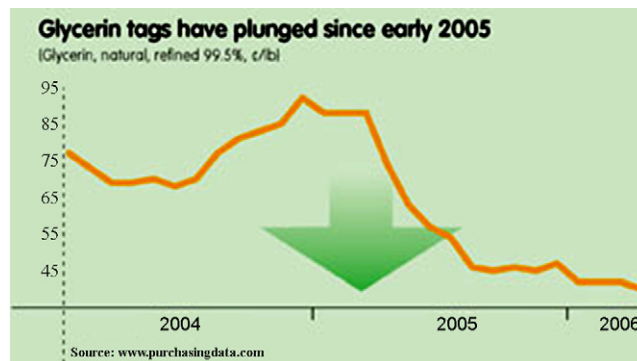


Fig. 3. Glycerol price trend [3].

glycerol surplus [9]. This scenario would give poor visual image of glycerol by-product towards viability and economy of biodiesel and biorefineries production [11], market price stability of current crude glycerol as well as environment due to improper disposal of glycerol [12]. In tandem with this awareness, a lot of research and efforts have been considerably developed and continuously investigated to transform the low value glycerol by different strategies and approaches. The following topics would discuss on petroleum derived-oxygenate fuel additive and potentially promising value of glycerol to be transformed into fuel additive.

2. Fuel additive

Fuel additive which could be classified into gasoline/petrol [13] and diesel additive [14] is a chemical substance that assists the cleanliness of engine part, i.e. carburetor, intake valve and fuel injector, prevent incomplete combustion, temper fuel gelling and nozzle choking, as well as protect engine parts from corrosion which leads to better engine performance and acceleration, improve fuel economy and reduce emissions of greenhouse gas [15]. Composition of diesel fuel, alcohol and fuel additive likewise could indigenously reduce the particulate emissions [16] while addition of additive to marine diesel fuel could significantly reduce particulate emission, emission concentration of CO₂ and NO, in the meantime improve the emission concentration of oxygen and excess air quantity [17]. The composition of additive in jet fuel between about 1 and 70 wt% could improve the thermal stability and reduce deposits in jet engine [18].

Various types of fuel additive derived from petroleum as well as biomass feedstock which could be classified into metal-based [19–21], oxygenates [22–26], wax dispersant [27], nitrogenates [28], antiknock agents [29,30], lead scavengers and fuel dyes [31] are generally will be added in small amount of concentration to neat or blended fuel [14]. Ever since The U.S. Clean Air Act Amendments of 1990 has called for reformulated and oxygenated gasoline, a lot of research and development on fuel additive was invested to meet the even tighter future emissions specifications of sulfur, olefins, vapor pressure, soot and smog reduction [32]. Diesel engine especially suffers from producing soot, particles and nitrogen oxide has shown improvement with oxygenate additives in a study conducted by Satgé de Caro et al. [33].

2.1. Oxygenate additive

Oxygenate compound could assist in octane rating increment and combustion quality that reduce particulate emission and carbon monoxide production. The molecular structure, local oxygen concentration and content of fuel could influence the reduction amount of particulate emissions [14]. Marchetti et al. [24] also reported that fuel containing 10–25% (v/v) oxygenate

could effectively reduce particulate emission. The oxygenate additives commonly used are alcohol, ether and ester functional groups. For alcohol, methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), propanol ($\text{C}_3\text{H}_7\text{OH}$) and butanol ($\text{C}_4\text{H}_9\text{OH}$) can be used in motor fuels. However, only the first two alcohols are widely available and technically economical to be used for internal combustion engine (ICE) [34].

Ethanol, familiarly termed as bioethanol is biologically produced from fermentation and hydrolysis derived from renewable sources of feedstock such as wheat, sugar beet, corn, straw, and wood [35–40]. Ethanol has been attractively deployed as oxygenate additive to gasoline for its major advantages in significantly reducing visible smoke and particulate emissions, enhancing engine thermal efficiency, and overall reduction in emission of carbon dioxide and other greenhouse gaseous [35,37,41]. However, bioethanol vaporize more easily which can be potential ozone layer aggravation agent [37] and it also increase the emission of aldehydes [41–43] and acetic acid [42,44]. According to He et al. [41], the exhaust emission is much influenced by ethanol content and gasoline engine operating conditions. They have done series of study of regulated and unregulated emissions from spark ignition engine to observe the emissions of CO, THC and NO_x correlate to the relationship between air/fuel equivalence ratio and brake mean effective pressure (BMEP). Besides, there were also studies reported on the emissions from diesel engine exhaust in conjunction with catalyst efficacy and engine operating conditions [45–47]. It seems that the reduction of exhaust emissions has now been a major research not only for catalyst design but also engine development. It is important to note, nevertheless, that ethanol tend to separate and immiscible in diesel fuel [33,48], which make its drawback as a gambit to other chemical building blocks as fuel additive.

Methanol can be synthesized from natural gas and biomass via partial oxidation reaction which is costly intensive. A study was conducted to investigate the engine performance and emissions of the oxygenated methanol-fuel blends under various fuel delivery advance angles in a compression ignition engine [23]. Although methanol is considerably easier to be found than ethanol, it is still less preferred due to less environmentally benign fuel and more readily ignited in hot surface which leads to pre-ignition and knocking in engine [34].

Methyl tertiary butyl ether (MTBE), in 1979, had been widely used as octane booster in gasoline component. It is commercially manufactured via chemical reaction of methanol and isobutylene [49]. This ether could easily meet the 2% oxygen requirement for RFG. For over 20 years, this oxygenate had been used in the gasoline blending pool since it was the most economical oxygenate that refiners could use to contain RFG manufacturing costs [50]. However, this oxygenate compound was considerably thought as health risk threat by International Agency of Research on Cancer (IARC) and Environmental Protection Agency (EPA) [51] in 2000. Although the adverse effects of MTBE ingestion are still not fully understood, National Science and Technology Council (NSTC) has outlined and assessed the effect of MTBE towards air, water, fuel and engine performance as well as health, which could be summarized as below [43]:

- (a) Despite reduction of toxic emission, MTBE could increase emission of hydrocarbon compound which is formaldehyde, which is toxic, allergenic and carcinogenic.
- (b) MTBE gives unpleasant taste even in very low concentration. In Santa Monica, California, concentration of MTBE rendered the shutdown of a drinking-water production well or well-field which released from underground gasoline storage tank. Alkyl ether oxygenates are much less biodegradable than ethanol or other aromatic hydrocarbon constitute of gasoline, and therefore would persist longer in ground water.

- (c) It gives no significant difference on engine performance but there is reduction on fuel economy around 2–3%.
- (d) Acute symptom of headaches, nausea, dizziness and breathing difficulties associated with MTBE in gasoline. However, the data is too limited to draw quantitative estimate of the full range and distribution MTBE exposures among the general population. Assessment also found that chronic non-cancer health effects would not likely to occur at environmental or occupational exposures to MTBE.

Hitherto, numerous modeling studies, sampling investigations and analytical techniques have been conducted to gain comprehensive data on the environmental ramifications and human health exposure of MTBE and other alkyl ether oxygenate compounds, i.e. ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME), tertiary hexyl methyl ether (THEME), diisopropyl ether (DIPE), in such large quantities [49,52–60]. This, ostensibly, has gain impetus among scientists and researchers as well to investigate the MTBE and other oxygenated fuel additive degradation behavior and treatment through biological [61–63] and chemical approach [64–67], e.g. by means of enzyme and bacterial strain biocatalysts, as well as air stripping, carbon adsorption, ultraviolet/ H_2O_2 and $\text{O}_3/\text{H}_2\text{O}_2$ advanced oxidation processes. Besides, the omnipresence of other types of oxygenate fuel additive, i.e. 2-methoxyethyl acetate (MEA), 1,1-diethoxyethane, and dimethyl ether (DME), has driven the research of exhaust emission improvement of NO_x and particulate matter as well as effects on diesel engine combustion [68–71]. Few reports have been found on NO_x emission reduction using ethanol fuel additive. There is also a report on biodegradation behavior of potential fuel additive of dibutyl maleate (DBM) and tripropylene glycol methyl ether (TGME) [24].

3. Glycerol

Glycerol is the simplest trihydric alcohol which has IUPAC name of propane-1,2,3-triol. It is also commercially known as glycerin, 1,2,3-propanetriol, 1,2,3-trihydroxypropane, glyceritol or glycyol alcohol. Pure glycerol is colourless, odorless, viscous liquid with syrupy and sweet taste. As shown in Fig. 4, glycerol has three hydrophilic hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature [72,73]. Table 1 lists physical and chemical properties of glycerol which is importantly associates to its application.

Glycerol was first discovered by Swedish researcher, K.W. Scheele in 1779 who obtained substances with sweet taste from heated reaction of olive oil with lead oxide. In 1811, Michel Eugene Chevreul, a French chemist called the sweet liquid as glycerin and thereafter defined fatty acids ethereous chemical formulas as well as glycerin formulas in vegetable oils and animal fats. His work on producing fatty acids from reaction of fatty materials with lime and alkali was patented, and to some extent, the first industrial method of getting glycerin from neutral fats oxyhydroxide saponified with further glycerin extracted from soap leaches was discovered [74]. Such discovery has offered astounding advancement towards glycerin purification and application to various products. Today, glycerol has been widely used in food and beverages, feedstock for raw chemicals, research and laboratory usage and pharmaceutical applications [75]. The wide realm of glycerol applications are suggested in Table 2, which are transformed by either biological or chemical reactions.

The potential for bacteriologic transformation of glycerol into products that can be used for plastic production has been demonstrated [12]. The recent work by Yang et al. [76] has successfully converted the crude glycerol by fermentation to obtained up to 83.56 g 1,3-propanediol with a yield of 0.62 mol/

Table 1

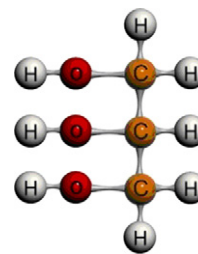
Physical and chemical properties of glycerol [72].

Properties	Values	
Chemical formula	$\text{CH}_2\text{OH}-\text{CHOH}-\text{CH}_2\text{OH}$	
Formula weight	92.09	
Form and colour	Colourless and liquid	
Specific gravity	1.260 ^{50/4}	
Melting point	17.9 °C	
Boiling point	290 °C	
Solubility in 100 parts		
Water	Infinitely	
Alcohol	Infinitely	
Ether	Insoluble	
Vapor pressure in 760 mmHg	290 °C	
Heat of fusion at 18.07 °C	47.49 cal/g	
Viscosity liquid glycerol		
100%	10 cP	
50%	25 cP	
Diffusivity in	(DL × 10 ⁵ sq cm/s)	
<i>i</i> -Amyl alcohol	0.12	
Ethanol	0.56	
Water	0.94	
Specific heat glycerol in aqueous solution (mol%)	15 °C (cal/g °C)	30 °C (cal/g °C)
2.12	0.961	0.960
4.66	0.929	0.924
11.5	0.851	0.841
22.7	0.765	0.758
43.9	0.670	0.672
100	0.555	0.576

mol glycerol and productivity of 1.61 g/L/h with *K. oxytoca* M5a1 bacteria. The use of bacteriologic transformation of glycerol also has been evidently demonstrated for the production of dihydroxyacetone for cosmetic applications [77], succinic acid [78] and citric acid [79] for food and pharmaceutical industries, polyhydroxyacanoate for medical and agricultural field [80] as well as other products for basic chemical applications. In addition to biological method, chemical transformation is another approach to convert glycerol to more valuable products which includes selective oxidation, hydrogenolysis, dehydration, acetylation, carboxylation, decomposition, dehydroxylation, selective oligomerization, reforming towards syngas, esterification and etherification. The transformation of glycerol into fuel oxygenates by etherification [81–83] and esterification methods [84,85] are among chemical reactions that draw interest of many researches since they are economically beneficial to the production of glycerol by-product and biodiesel process.

One of its potential and promising values has been envisioned for the automotive and biorefinery industries—to transform it into fuel additive. Glycerol ethers [26,82], acetyl glycerol [86–89] and glycerol acetal [90–92] have been identified as valuable replacement of fuel additive which depends on depleting sources, price uncertainty and growing environmental concern of petroleum feedstock. These glycerol-based fuel additive are excellent additives with large potential for diesel and biodiesel formulation that assist to a decreasing in particles, hydrocarbons, carbon monoxide and unregulated aldehydes emissions [93]. Moreover, they can act as cold flow improvers and viscosity reducer for use in biodiesel [94] and as antiknock additives for gasoline [89,95]. This issue is of significant importance due to the growing demand of new additives specifically for biodiesel that are biodegradable, non-toxic and renewable. In addition, these derivatives can also be used as octane boosters for gasoline, as an alternative to commercial trialkylethers (MTBE and ETBE) [96].

Glycerol ether produced from etherification of glycerol has commercialization potential by ratio blending with gasoline, diesel

**Fig. 4.** Molecular structure of glycerol.

fuel, marine diesel fuel and jet fuel [97]. Appropriate ratio of glycerol ether, alcohol and gasoline, for example, could reduce vapor pressure to desired level and reduce fuel consumption [98]. In addition to those advantages, the presence of glycerol ether in all types of fuel compositions as fuel additives could help lower the gel temperature of fuel which leads to viscosity reduction. The presence of hydroxyl groups on partially etherified glycerol derivatives could also lower the NO_x emission [99].

Higher glycerol ether [97,100–102], acetyl glycerol [87,89] and glycerol acetal [90,91] have been identified as potentially valuable additives for diesel, gasoline, biodiesel and blend biodiesel–diesel. The new route chemistry of glycerol-based additive seems to catch the motivation and interest of many researchers lately, in which the utmost importance could be summarized as follows:

- As an effort to redeem glycerine surplus and glut situation which might ruin the economy and market of glycerol as well as biodiesel/biofuel refinery and oleochemical industries since glycerol synthesis and by-production are closely linked to these industries. The innovative development of glycerol-based fuel additive could positively advance the production of biodiesel at small to moderate scale facilities, expand the product market and increase revenue of biofuel industries.
- As a renewable sources and bio-based product, that is biodegradable, green refinery process and great environmental value demanded by modern society who favors the non-dependence on depleting sources of petroleum and fossil fuel feedstock. This alternative feedstock chemical of glycerol could play essential component in the advancement of integrated biorefinery industries as well as cleanliness of environmental life cycle.
- As high quality additive that offers valuable and economical fuel towards engine efficiency and environmental compliance. Glycerol-based additive has been reported to have be able to enhance cold and viscosity properties of liquid fuels, as antiknock additives for gasoline, boost octane rating, decrease fuel cloud point (CP), reduce greenhouse gas emissions and could replace the controversial tertiary alkyl ether (MTBE and ETBE).

Fig. 5 depicts the interrelation of glycerol-based additives importance towards biorefinery industry, engine performance, environment and society. Despite those fascinating commercial advantages, durability and reusability of novel catalysts which could lead to high product yield and selectivity within low range of reaction temperature and time are still remain as challenges which require rigorous investigation and development. Hence, this paper will review the extensive foregoing works associate to glycerol transformation into fuel additive for the wider scope of future studies.

4. Glycerol transformation into fuel additives

Without modifying and deriving glycerol makes it incompatible if being added directly to fuel due to its decomposition and

Table 2
Various applications of glycerol.

Product	Reaction	Usage
1,3-Propanediol	Glycerol fermentation by <i>Klebsiella Pneumoniae</i> [110] Glycerol selective dehydroxylation [111]	Use as a monomer in the synthesis of several polyesters such polytrimethylene terephthalate (PTT) and polyethylene terephthalate (PET)
Propylene glycol	Glycerol hydrogenolysis [110]	Mainly applied to unsaturated polyester, antifreeze liquid, and additives for liquid detergent
Docosahexaenoic acid (DHA)	Crude glycerol with microalgal culture [112]	Important omega-3 polyunsaturated fatty acid (v-3 PUFA) with medically established therapeutic capabilities against cardiovascular diseases, cancers, schizophrenia, and Alzheimers, also an essential nutrient during early human development
Glycerol carbonate	Glycerol with CO ₂ [113]	Prominent role as the monomer could be used for the synthesis of new functionalized polymers that might have interesting new applications
Dichloropropanol (DCP)	Glycerol with heteropolyacid [114] Glycerol reaction with hydrochloric acid catalyzed by acetic acid as acid catalyst [115]	Chemical feedstock for organic compounds, monomers and reactants for producing plastics
Butanol	Glycerol fermentation by <i>Clostridium pasteurianum</i> [116]	Potential biofuel which could be used for gasoline/petroleum without changes in engine design As a solvent for chemical and textile process, organic synthesis and chemical intermediate, as well as coating applications Use as paint thinner Use as hydraulic and brake fluids Use as perfume base
Ethanol	Glycerol fermentation by <i>E. coli</i> [4]	Largely use as fuel and fuel additive, also a fuel for bipropellant rocket Fuel to power direct ethanol fuel cells to produce electricity and by-product H ₂ O and CO ₂ Main constituent in alcoholic beverages Chemical feedstock for organic compounds such as ethyl halides, ethyl ester, acetic acid, butadiene, ethyl amines, diethyl ether Use in medical application as antiseptic and antidote for poisonous and toxic chemicals
Hydrogen	Glycerol aqueous phase reforming by Ni–Sn catalyst [117] Glycerol steam reforming process by Ni [118] Glycerol aqueous phase reforming by supported metal catalyst [119] Glycerol steam reforming by ceria-supported metal catalyst [120]	Efficient devices for the production of electrical power
Acrolein	Reaction gas phase glycerol/water mixture by zeolite [121] Glycerol conversion on hot compressed water [122] Glycerol dehydration by micro- and mesoporous ZSM-5 [123] Glycerol dehydration over silica-supported heteropolyacids [124] Glycerol dehydration over activated carbon-supported silicotungstic acids [125]	Use to produce acrylic acid, acrylic acid esters, super absorber polymers, and detergents
Succinic acids	Glycerol fermentation by <i>Anaerobiospirillum succiniciproducens</i> [126]	Used for the manufacture of synthetic resins and biodegradable polymers and as an intermediate for chemical synthesis
Dihydroxyacetone	Glycerol oxidation catalyzed by gold catalyst in multiphase structured reactors [127] Glycerol oxidation over carbon-supported gold catalyst [128] Glycerol oxidation with <i>Gluconobacter Oxydans</i> [129] Electrocatalytic glycerol oxidation [130]	Used in cosmetics industries as a tanning agent

polymerization nature. Thus, this could invite consequential engine problems at high temperatures. An active study on glycerol-based additive, mono-tertiary butyl glycerol ether (MTBG), was first done by Malinavskii and Vvedenskii back in 1953 [103]. Since then, the spectrum research and development on glycerol-based additive has been a continuum.

From open literature, the transformation of glycerol to glycerol-based additive could be processed through several chemistry routes:

1. Reaction of glycerol with acetic acid through acetylation or esterification process.
2. Reaction of glycerol with ether substrate through etherification process.
3. Reaction of glycerol with glycerol through etherification process.
4. Reaction of glycerol with acetone and acid anhydride through acetalation process.

As mentioned earlier, glycerol-based additive is capable of demonstrating tremendous good quality towards engine performance and environmental requirement. Focus for the glycerol transformation into fuel additive has been mainly on physical properties, reaction mechanism, catalyst design, operating condi-

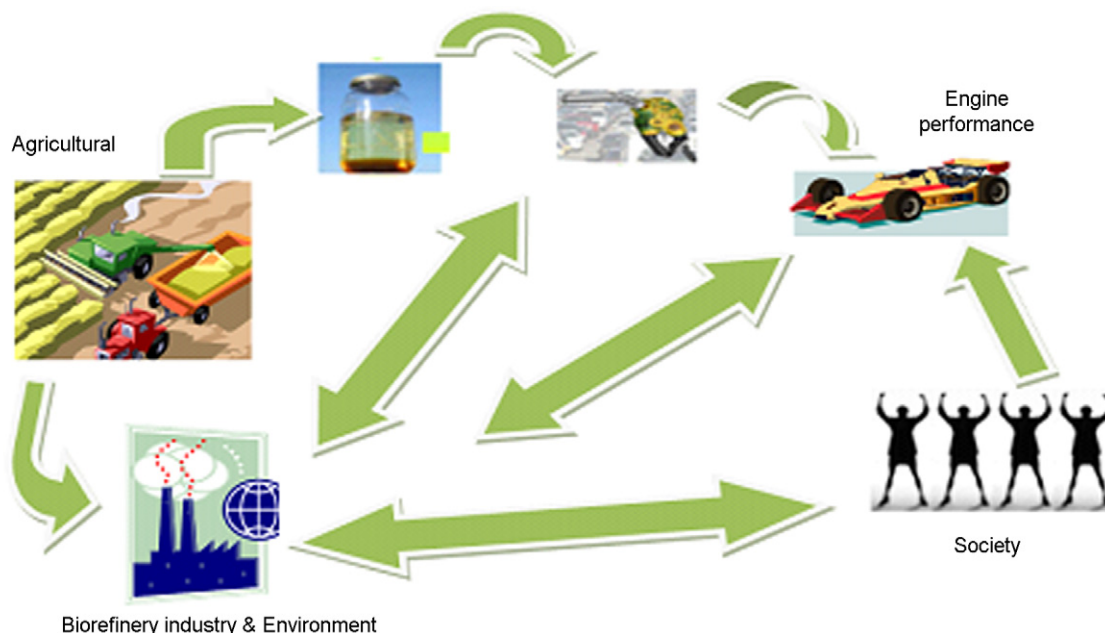


Fig. 5. Importance and interrelation of glycerol-based fuel additive.

tions of temperature, pressure, addition of solvent or precursor, etc., in which most of it will be reviewed here.

4.1. Physical properties

The physical properties of fuel additive obtained from the reaction of acetalation, etherification and acetylation is essentially important to be characterized to determine, i.e. its solubility in biodiesel/diesel/gasoline and the effect of fuel additive properties towards the fuel (biodiesel/gasoline/diesel) vapor pressure, cloud point (CP), pour point, specific gravity and viscosity. Table 3 lists down the standard methods used for characterization of physical properties of fuel additive. There are limited reports on the research work of glycerol-based additive physical properties characterization. Nevertheless, the available reports are going to be reviewed here for beneficial reference of other and future research work.

Noureddini and co-workers [101,104] who studied glycerol reaction with isobutylene published the physical properties of 24% monoethers, 62% diethers and 14% triethers using 100% neat methyl esters, 100% diesel and various blends of diesel and methyl esters. They briefly described that the glycerol ether showed no solubility at all in all fuel blends up to 22 wt.%, demonstrated its potential as cloud point depressant, improved pour point of fuel, displayed negligible impact on fuel specific gravity and decreased

the viscosity of neat methyl esters and biofuel blends. In other glycerol etherification research work, Karinen and Kraus [104] reported that the glycerol ether obtained has octane numbers of 112–128 (BRON) and 91–99 (BMON) which is suitable for gasoline component.

A recent study from García et al. [105] who first characterized the glycerol acetal, denoted as acetal-1, which was resulted from reaction of glycerol and acetone, ostensibly did not meet the satisfying requirement of oxidation stability and flash point from both ASTM and EN Standard. Modifying acetal-1 with acetic anhydride to produce product mixture of acetal-2 and triacetin has led their work to a remarkable finding. Acetal-2 has been identified to be a viscosity improver, has better flash point and oxidation stability. They also found that acetal-2 did not improve cold properties as much as triacetin, but it did not give negative impact and did not increase density as much as triacetin.

4.2. Reaction mechanism

General or typical reaction mechanisms of glycerol reaction to produce typical glycerol-based additive products are presented here, without specifying any specific catalyst types and reaction conditions. Basically, the hydroxyl group of glycerol molecule will be protonated in the presence of heat or catalysts, which makes glycerol molecule ready to accept electron from the donors. The donors in this review are confined to isobutylene, acetic acid, acetone, acetic anhydride and glycerol itself. Table 4 lists down the general reaction mechanisms of glycerol to produce glycerol-based additive.

It is important to note that the reaction of glycerol with isobutylene would produce mono-*tert*-butyl glycerol ether, di-*tert*-butyl glycerol ether and tri-*tert*-butyl glycerol ether. Nonetheless, only higher ethers, di-*tert*-butyl glycerol and tri-*tert*-butyl glycerol, are considered to be quality fuel additive for their specialties to reduce contaminant emissions, as alternative additives for alkylethers and other advantages that are shown in Table 5. Moreover, mono-*tert*-butyl glycerol has been reported as highly water soluble which is not suitable for diesel blending agent. The same reason goes to higher acetyl glycerol, diacetyl and triacetyl glycerol which have shown as valuable fuel additives to enhance

Table 3
Standard methods of fuel additive physical properties characterization.

Physical properties	ASTM	EN	AOCS
Density	D5002-94 [132]	14214, 590 [105]	
Heat of combustion	D240-92 [132]		
Cloud point	D2500-91 [103,132]		
Pour point	D97-96a [103,132]		
Flash point		14214, 590 [105]	
Oxidation stability		ISO 12205 [105]	
Viscosity	D6751, D445-96, D446-93 [103,132]	14214 [105]	
Vapor pressure	D5191-96 [103,132]		
Acid value			Te 2a-64 [132]
Iodine value			1c-85 [132]

Table 4

General reaction mechanisms of glycerol to produce glycerol-based fuel additives.

Reaction	General mechanism
Etherification [5]	<p>The scheme shows the stepwise etherification of glycerol (G) with isobutylene (IB). 1. Glycerol (G) reacts with IB to form MTBG1 and MTBG2. 2. MTBG1 and MTBG2 react with IB to form DTBG1 and DTBG2. 3. DTBG1 and DTBG2 react with IB to form TTBG. Chemical structures are provided for each species, showing the progressive substitution of hydroxyl groups with tert-butyl ether groups.</p>
Etherification [107]	<p>The scheme illustrates the polymerization of glycerol: 2 Glycerol → Diglycerol + H₂O Diglycerol + glycerol → Triglycerol + H₂O Triglycerol → [Polyglycerols] Chemical structures for glycerol, diglycerol, and triglycerol are shown.</p>
Acetylation [89]	<p>The scheme shows the acetylation of glycerol with acetic acid: Glycerol + Acetic Acid → Monoacetylglycerols (MAG) MAG + Acetic Acid → Diacetylglycerols (DAG) DAG + Acetic Acid → Triacetylglycerol (TAG) + H₂O Chemical structures for glycerol, acetic acid, MAG, DAG, and TAG are provided.</p>

Table 4 (Continued)

Reaction	General mechanism
Acetalation [107]	<p style="text-align: center;"> <chem>HOCH2CH(OH)CH2OH + CC(=O)C >> [1] >> [2] >> [3]</chem> </p> <p style="text-align: center;"> Acetone Acetic anhydrid </p>

cold properties, reduce viscosity for diesel fuel and act as antiknock with gasoline. Therefore, the most challenging in glycerol transformation into fuel additives is to obtain high selectivity of desired product with high conversion of glycerol.

4.3. Influence of catalyst

Different types of heterogeneous solid catalysts have been studied such as ion exchange resins, zeolites, polysaccharide derived mesoporous material, mesoporous silica, carbonate based and alkaline earth metal. Those studies are mainly revolved around the effect of acidity, basicity, porosity, catalyst loading, different techniques of catalyst preparation and its reusability.

Melero et al. [5] have studied the acidity of sulfonic functionalized mesoporous silica towards catalytic behavior of glycerol reaction with isobutylene. From both works of comparison on different sulfonic acid mesostructured silica and other commercial sulfonic resins, they found that with the combination of moderate temperatures and correct molar ratio of reaction feed, the moderately strong acid centers those located in arenesulfonic-acid-modified mesostructured silicas could provide improved results both in glycerol conversion and selectivity towards the desired products. In their other work, Melero et al. [89] also found that the acid strength of the sulfonic acid incorporated on mesoporous silica material was an important factor affecting the catalytic performance. An experiment involving specific activity per acid site showed that the increasing catalyst activity trends agreed with the increasing acid strength of sulfonic group propylsulfonic < arenesulfonic < fluorosulfonic. Nonetheless, Kle-

páčová et al. [100] who investigated the catalyst activity and selectivity from different types of catalyst observed the close relation of acid strength towards catalytic activity could only be concluded from comparison of its own kind of catalyst. The difference of 10% initial reaction rate over ion exchange catalyst between Amberlyst-35 and Amberlyst-15 was due to 10% higher acidity strength of Amberlyst-35 than that of Amberlyst-15. The same conclusion was also made towards zeolite H-Beta and H-Y. However, the acid strength comparison between ion exchange resin and large pore zeolite seemed not to give the same conclusion. It was found that the higher total acidity of ion exchange resin for nearly five times than that of zeolites did not responsible for the difference of initial reaction rate of these two types of catalysts due to their other catalytic properties [100].

Ferreira et al. [86] used dodecamolybdophosphoric acid ($H_3PMo_{12}O_{40}$) or PMo encaged in NaUSY zeolites loaded with different amount of heteropoly acid (HPA) to test the effect of catalyst loading on glycerol reaction with acetic acid. The catalytic activity appeared to enhance with the higher content of HPA loading up to a certain amount of PMo-NaUSY, in which after this point, the higher loading of HPA content would suppress the catalytic activity due to decrement of surface area and microporous volume that further lead to internal diffusion limitation.

There were also studies on the effect of basicity and Lewis acidity balance of catalyst. Agnieszka et al. [106] firstly discovered that glycerol conversion increased with increasing catalyst basicity, which was increasing in the order: $MgO < CaO < SrO < BaO$. However, further investigation has lead to another finding on the roles of Lewis acidity of CaO-based catalyst on high glycerol

Table 5

Glycerol reaction with different types of substrate, the corresponding products and commercial values.

Substrates	Transformation process	Glycerol-based additive	Commercial value	Reference
Isobutylene	Etherification	di- <i>tert</i> -Butyl glycerol ether tri- <i>tert</i> -butyl glycerol ether	1. As diesel and biodiesel reformulation 2. Improve cold properties 3. Reduce contaminant emissions of particulate matter, hydrocarbons, carbon monoxide and unregulated aldehydes 4. Reduce fuel viscosity 5. Octane boosters 6. Alternative to commercial tertiary alkylethers (MTBE and ETBE) 7. Decrease cloud point of diesel fuel when blend with biodiesel 8. Good properties as blending components and good solubility in diesel	[5,89], [100], [131], [103], [105]
Acetic acid	Acetylation/esterification	Diacetyl glycerol Triacetyl glycerol	1. Improve the cold and viscosity properties of liquid fuels (including biodiesel) 2. As antiknock additives for gasoline	[87,89] [86,88]
Glycerol	Etherification	Polyglycerol	Excellent lubricity	[107]
Acetone and consequently acetic anhydride	Acetalation	Acetal glycerol Triacetyl glycerol	1. Oxidatively stable 2. Viscosity improver 3. Does not increase density of fuel	[105]

etherification conversion. Their investigations on various CaO-based material tests concluded that the surface, both basic and acid site of catalyst properties with correct balance of basicity and Lewis acidity possessed the highest catalytic activity. Theoretically, the presence of acidic catalyst would make the glycerol hydroxyl group protonated and cause it a good leaving group. It is followed by the nucleophilic attack of a hydroxy group of another glycerol or substrate ether molecule, depends on substrate feed, accompanied by the leasing of water molecule that eventually leads to the deprotonated ether formation, yielding the respective di-, tri-, polyglycerol or glycerol ether. The explanation of base-catalyzed glycerol etherification is still in the postulation phase, in which more investigations need to be discovered to confirm on the postulation of very high temperature and other surface groups of the catalytic solid participated in the reaction mechanism that cause the hydroxyl group is a sufficiently good leaving group [93,106].

Mesoporous materials apparently have been widely employed either as catalyst support or directly involved as catalyst. A comprehensive study by Luque et al. [88] on sulphonated Starbon[®] (Starbon[®]-400-SO₃H) as polysaccharide derived mesoporous interestingly showed a similar activity to that of sulphonated silica material and better performance than that of beta zeolites and *p*-toluenesulfonic acid (*p*-TSA) in glycerol etherification with isobutylene [88]. In other study of mesoporous material, different techniques of adding different alkaline earth elements to mesoporous MCM-41 by incorporation, impregnation and exchange have been studied by Clacens et al. [107]. They observed that cesium impregnated on pure mesoporous silica was the best compromise between activity, selectivity and catalyst leaching. At a conversion of 80%, such catalysts have a very high selectivity to [di- + triglycerol] of 90%. Even though cesium exchanged catalyst demonstrated as the most stable catalyst, but cesium impregnated could be reused without major modification on the selectivity. The mesoporous structure of MCM-41 was observed remained in good condition despite the impregnation method and catalyst leaching, which explained the stable selectivity of cesium impregnation mesoporous catalyst [107,108] (Table 6).

Klepáčová et al. [100,102] investigated the difference type of catalysts between ion exchange resins Amberlyst-15 and -35 and large pore zeolites H-Y and H-Beta. From the comparison, it can be seen that the highest yield of desired di- and triethers of glycerol was obtained over ion exchange resins at 60 °C (86.6% on Amberlyst-15 and 88.7% on Amberlyst-35, respectively) after 8 h of etherification reaction. There was no tri-ether glycerol formation over H-Beta zeolite and low selectivity over H-Y zeolite. It could be concluded that because of high degree crosslinking structure, the Amberlyst-35 catalyst was identified the most active and selective [100].

Gonc lves et al. [87] who also studied different solid acid catalysts, i.e. Amberlyst-15, K-10 montmorillonite, niobic acid, HZSM-5 and HUSY in glycerol reaction with acetic acid observed that Amberlyst-15 was the most active and selective catalyst, with conversion of 97%, selectivity of 54% to diacetin, 31% to monoacetin and 13% to triacetin after 30 min reaction. The strength of acid sites on the catalysts was not the factor of this behavior, since zeolite was the highest acid strength but the worst found in this study. Pore distribution and hydrophobicity properties were the main respective reason for the diffusion limitation and acid site deactivation by water suppression [87]. The same conclusion was also made by Luque et al. [88] who did a comparison between different acid catalyst H₂SO₄, sulphated zirconia and newly developed mesoporous Starbon[®]-400-SO₃H. It was deemed that the porosity distribution of the Starbon[®] material that really explained the outstanding glycerol conversion and product selectivity over other types of catalysts.

Richter et al. [109] investigated the influence of catalyst amount towards the reaction conversion and selectivity. It was found that, the increment of catalyst amount up to 0.4 wt.% had increased the conversion rate up to 20% from 10%. However, the increment of catalyst amount did not influence the selectivity of glycerol etherification reaction. Back in 1998, Nouredini et al. [103] investigated the effect of catalyst loading on glycerol etherification with isobutylene at 93 °C, molar ratio of 3:1 for 4 h. They did find out that the conversion was increasing with the increment of catalyst loading. However the product concentration was leveled off at catalyst loading of 5 wt% and glycerol was almost fully converted in 4 h.

Impregnated cesium on mesoporous aluminosilica was tested for its reusability towards glycerol conversion and product selectivity. It was shown in Fig. 6 that the reuse catalyst has lower activity than that of initial catalyst condition, due to difference in cesium content, in which had reported by Clacens et al. [107] that different amount of impregnated cesium on mesoporous aluminosilica would impact on glycerol conversion. However, the selectivity to di- and triglycerol were comparably equal demonstrated by both catalyst states as displayed in Fig. 7.

4.4. Influence of reactant

Most works were done on the variation of molar ratio of reactant, comparison with other types of substrates as one of the reactants or precursor, and addition of solvent to observe the influence on catalytic behavior and product distribution.

The influence of reactant stoichiometry was described by Nouredini et al. [103] for glycerol etherification at reaction temperature of 80 °C and 93 °C. The conversion of glycerol appeared to enhance with the increment of molar ratio isobutylene to glycerol (IB/GLY) at both reaction temperature [103]. In one of the experiments, Karinen and Kraus [104] also studied the effect of different initial molar ratio of isobutylene to glycerol towards conversion and selectivity. They found that higher molar ratio IB/GLY than 3 at temperature of above 70 °C had almost complete of glycerol conversion. This was not the case for lower initial molar ratio at temperature of 80 °C, in which the slower rate of conversion caused by higher viscosity of higher content of glycerol, thus affected the mass transfer between phases and catalyst. Lower initial molar ratio also could cause lower selectivity and invited other side reaction to occur. This could be explained by availability of isobutene in slower mass transfer phases to react more easily in the oligomerization reaction. Enhancement of IB/GLY ratio would decrease viscosity, hence, offered easier mass transfer between phases that could reach a maximum selectivity. Nevertheless, as the ratio was increased further, relatively more isobutene was available and more oligomerization to be occurred.

The employment of predictive equation obtained by factorial design of experiment has helped the determination of reactant stoichiometry or temperature influential towards glycerol conversion in acetylation reaction. From data computation by the equation, it demonstrated that the acetic acid to glycerol molar ratio (AA/GLY) was the more influential factor on the glycerol conversion than that of the temperature. An enhanced of glycerol conversion was observed with the increasing acetic acid loading for all temperatures, whereas the detrimental effect of temperature increment was identified at low loadings of acetic acid [89]. The optimization of molar ratio of reactant towards selectivity was studied intensively by Luque et al. [88] using Starbon[®] catalyst under microwave irradiation condition, keeping the amount of catalyst and temperature constant, but simultaneously varying the reaction time and irradiation power. They found that the formation of monoacetylglycerol was favored towards the low molar ratio of 1:1 acetic acid to glycerol, at short reaction time of 10 min and

Table 6

Catalyst, glycerol conversion and product selectivity of glycerol reactions into fuel additive.

Reaction	Catalyst	Glycerol conversion	Selectivity	Remarks	Reference
Etherification (reaction of glycerol with isobutylene)	Ar-SBA-15 and other sulfonic functionalized mesostructured silica	100%	DTBG + TTBG ~ 90%	Sulfonic acid-functionalized mesostructured displayed comparable result towards commercial acid resin catalyst, SAC-13. The optimal conditions achieved for the mentioned glycerol conversion and product selectivity's are at 75 °C, molar ratio IB:GLY of 4:1 and 4 h of reaction time	[5]
	Polysaccharide derived mesoporous materials,	66%	MTBG >99%	The catalyst used at 0.1 g, IB:GLY ratio of 1:3, 300 W, 100–120 °C and 15 min reaction time had favored the formation of monother, which has least desirable qualities for fuel additive.	[88]
	Starbon [®] -400-SO ₃ H Amberlyst-35	68%	TTBG, not indicate in figures	Investigation on different types of catalyst which included H-Y zeolites, H-beta zeolites, <i>p</i> -toluenesulfonic, Amberlyst-15 and Amberlyst-35. Amberlyst-35 was identified as the best catalyst toward conversion and selectivity. Other studies investigated were the influence of water and solvent. The optimal temperature for the best conversion and selectivity was 60 °C.	[100]
	Amberlyst-35	>95%	At 80 °C and molar ratio IB:GLY of 4.5 TTBG ~47%, DTBG ~ 50% and MTBG ~ 3%	Adjusting and controlling the reaction condition could control the product distribution. The formation of triethers could be obtained with high initial molar ratio IB:GLY. While the formation of diethers would favor at 80 °C and stoichiometric molar ratio. Low conversion and low initial molar ratio would offer monoethers as main product.	[104]
Etherification (glycerol as sole reactant)	Cesium impregnated MCM-41 mesoporous catalyst	80%	Diglycerol + tri glycerol ~ 90%	Different techniques of catalyst preparation were investigated to find the most stable catalyst with high activity, conversion and selectivity. Cesium impregnated on MCM-41 mesoporous catalyst was found to be the best element and method.	[107,108]
	CaO-based	~90%	Diglycerol ~ 52% triglycerol ~ 48%	The strong basic and Lewis acid sites and catalyst material with the right balance of basicity and Lewis acidity offer high activity of glycerol etherification over alkaline earth metal oxide. The reaction condition was tested at 220 °C for 20 h of reaction time.	[106]
	Cesium hydrogencarbonate (CsHCO ₃)	100%	Diglycerol ~ 10%	The studies investigated the dependence of catalyst amount towards glycerol conversion and linear diglycerol selectivity. Different anion elements of cesium were also investigated to study the effect of basicity. The reaction condition was at 260 °C for up to 24 h of reaction time. It was found that high selectivity of linear diglycerol was obtained at low glycerol conversion and vice versa.	[109]
Acetylation/esterification (reaction of glycerol with acetic acid)	Amberlyst-15	97%	Diacetylglycerol ~ 54% triacetyl glycerol ~ 13%	Different solid acid catalysts were studied towards glycerol conversion and product selectivity. Amberlyst-15 was found to be the best catalyst while zeolite HZSM-5 and HUSY were the worst catalyst after 30 min at room temperature.	[87]
	Ar-SBA-15 F-SBA-15	~90%	Diacetylglycerol + triacetyl glycerol ~ 85%	The optimal condition found for high glycerol conversion and high selectivity was at 125 °C, AA:GLY molar ratio of 9:1 after 4 h of reaction over sulfonic acid-modified SBA-15, which demonstrate similar catalytic activity to ion resin catalyst.	[89]
	PMo immobilized NaUSY zeolite	68%	Diacetylglycerol ~ 59% triacetyl glycerol ~ 2%	Different loading of PMo from 0.6 wt% to 5.4 wt% was investigated to see the impact on conversion and selectivity. It was observed that PMo with 1.9 wt% showed the best catalytic behavior.	[86]
	Polysaccharide derived mesoporous materials, Starbon [®] -400-SO ₃ H	100%	Diacetylglycerol ~ 70% triacetyl glycerol ~ 75%	High selectivity towards respective monoacetin, diacetin and triacetin was observed with the control of the reaction condition. The optimal reaction conditions for diacetin selectivity were molar ratio of 3:1 AA:GLY, 300 W, 130 °C, 15 min, 0.2 g Starbon [®] -400-SO ₃ H.	[88]

100 W of irradiation power. However, higher molar ratio of acetic acid to glycerol, longer reaction time and higher irradiation power would favor the formation of diacetyl glycerol and triacetyl glycerol [106].

The addition of *tert*-butyl alcohol (TBA) was claimed could suppress the formation of isobutene oligomerization and improved selectivity towards ethers by elimination of mass transfer limitation between phases [104]. Ironically, the usage of TBA as

one of feed reactant quashed the selectivity towards ethers. This is due to the formation of water from TBA dehydration, which further causes hydrolysis reaction between water and ethers product formed. The influence of water towards catalytic activity is also reported by other research works [96,102].

In other work from Klepáčová et al. [100] who investigated the influence of solvent on etherification with isobutylene catalyzed by Amberlyst-35, remarked its utmost importance towards the

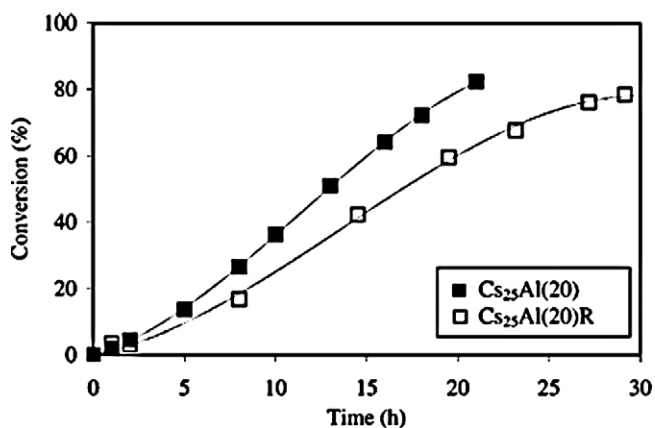


Fig. 6. Activity of the reuse catalyst [107].

reaction. The comparison of dioxane, sulfolane and dimethyl sulfoxide as reaction medium has witnessed a remarkable conversion percentage over dioxane, followed by sulfolane. The difference of conversion rate could be explained by the solubility properties, in which dioxane is more soluble in isobutylene than sulfolane. As for dimethyl sulfoxide, its partial negative charge due to polarization could deactivate ion exchange resin catalyst.

4.5. Influence of temperature

Temperature is arguably among the most important parameters that determine equilibrium mediated process regardless of solid catalyst being used, and thus is reviewed in this work as well to understand mainly on the effects towards glycerol conversion and selectivity.

The distinction impact of temperature towards reaction rate, conversion and selectivity has been discussed in most reports. Klepáčová et al. [102] investigated the influence of temperature-reaction towards glycerol conversion. They observed the highest conversion on 71.5% was achieved with the temperature of 60 °C and reaction time of 180 min. At higher temperature of 75 °C, glycerol conversion could achieve the highest of 71.3% within shorter reaction time. Further increasing the temperature would increase the reaction rate as well, but at the same time inviting an undesirable dealkylation of higher ethers (DTBG and TTBG) caused by the formation of lower ether (MTBG) and isobutylene. The same observation was also reported by Melero et al. [5]. The isobutylene split from higher ether would be oligomerised to form C₈ alkenes.

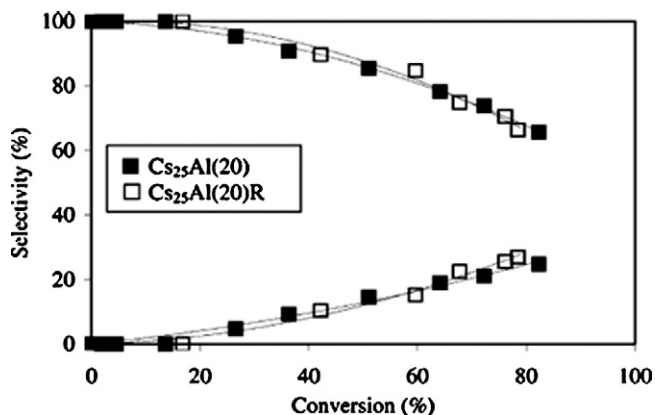


Fig. 7. Selectivity of the reuse catalyst [107].

This eventually caused redistribution equilibrium and decreased the conversion of glycerol [100].

The dealkylation of higher ether seems not to be only affected by higher temperature. It was reported by Nouredini et al. [103] who studied the temperature-molar ratio interaction, that at molar ratio of 3:1 IB/GLY, the C₈ formation decreased as a function of temperature. It was claimed that at low temperature and 3:1 reactant stoichiometry, higher ether formation was obtained and the catalyst favored the by-product formation. This has been agreed with another research work that reported the low temperature favored higher activation energy for oligomerization reaction rather than that of etherification [104]. Findings by Nouredini et al. [103] on dealkylation of higher ether at molar ratio 2:1, in which C₈ formation increased but higher ether formation decreased with the increment of temperature, further support their theory. Melero et al. [5] who studied molar ratio-temperature interaction also reported that high selectivity of DTBG and TTBG increased with higher molar ratio IB/GLY as a function of temperature. However, further increasing temperature would decrease the higher ether selectivity. They concluded that the optimal selectivity of higher ether was at 4:1 molar ratio and 75–85 °C. The low selectivity of higher ether at low molar ratio and low temperature was also elaborated by viscosity relevance, in which higher amount of glycerol caused high viscosity of reaction medium. Consequently, slow mass transfer between phases could temper the selectivity of higher ethers.

Glycerol conversion in reaction with acetic acid seemed to enhance with the increasing acetic acid loading for all temperature. Melero et al. [89] found that at low acetic acid loading, the detrimental effect of increasing temperature was significantly observed. They concluded the optimal condition for highest glycerol conversion was obtained with high molar ratio acetic acid to glycerol (AA:GLY) and low-medium temperature of 100–125 °C.

From the research work too, they observed that high molar ratio and high temperature quashed the formation of monoacetin (MAG). Intermediate molar ratio AA:GLY and high temperature was prone to the formation of diacetin (DAG) while high molar ratio and high temperature would influence the formation of triacetin (TAG). The molar ratio, ostensibly, was deemed to be the most influential parameter for formation of MAG, DAG and TAG [89]. The same pattern of selectivity was also observed from the research work of Luque et al. [88] who studied glycerol acetylation under microwave irradiation. At low irradiation power and shorter time, higher percentage of MAG formation was observed while at high irradiation power in addition to longer time and higher catalyst amount would favor the formation of TAG.

4.6. Influence of reaction time

Nouredini et al. [103] also investigated the effect of reaction time towards the reaction of glycerol etherification. At temperature of 93 °C, molar ratio IB:GLY of 3:1 and 5 wt.% of catalyst, reaction was reached equilibrium and all compositions were leveled off after 2 h. Even beyond 1 h of reaction, a slight decrease in ether formation and increase in by-product were observed. It has been deduced that when the equilibrium is reached, the free isobutylene will be consumed in the formation of 1- and 2-pentenenes. Beyond 3 h of reaction, the further formation of 1- and 2-pentenenes were in the expense of higher ether instead of isobutylene due to the complete reversibility of reaction [103]. The supposition is concurred by the findings from Klepáčová et al. [100] and Richter et al. [109], both of whom studied different types of catalysts and reaction conditions but found the same by-product occurrence at longer reaction time. Klepáčová et al. [102] reported that the formation of isobutylene dimers was proportional to the

reaction time of 8 h due to etherification equilibrium shifted towards lower ethers and glycerol by withdrawal of isobutylene. Whereas, Richter et al. [109] concluded that 40% of linear diglycerol was achieved during 6–12 h of reaction. However, at longer reaction time, diglycerol was consumed to form oligoglycerol.

5. Conclusion

The pitfalls of glycerol by-product excess production and the urge from modern society as well as government policy on renewable resources have motivated the research and development of glycerol as chemical feedstock of organic compounds into various applications. Glycerol-based additive has been identified to have particular qualities, which is suitable for blending agent in gasoline, biodiesel and diesel fuels. Several chemical routes of glycerol reaction into fuel additive and the advantages of every glycerol products are also described. Different concerted approaches and strategies of researchers are intentionally developed to investigate and study the influential of variable parameters, i.e. catalyst, temperature, reaction time, solvent and precursor, on the physical properties, conversion and selectivity of the glycerol-based fuel additive. Those studies are presented in this review paper and could be a reference for an extensive scope in the future studies.

Acknowledgement

Research University (RU) grant from Universiti Sains Malaysia is gratefully acknowledged.

References

- [1] Pramanik T, Tripathi S. Biodiesel: clean fuel of the future. *Hydrocarbon Process* 2005;84:49–54.
- [2] Bournay L, Casanave D, Delfort B, Hillion G, Chodorge JA. New heterogeneous process for biodiesel production: a way to improve the quality and the value of the crude glycerin produced by biodiesel plants. *Catal Today* 2005;106:190–2.
- [3] Woo C. Clean fuel trends in Asia: contribution of MTBE. *Hydrocarbon Process* 2007;86:85–8.
- [4] Yazdani SS, Gonzalez R. Anaerobic fermentation of glycerol: a path to economic viability for the biofuels industry. *Curr Opin Biotechnol* 2007;18:213–9.
- [5] Melero JA, Vicente G, Morales G. Acid-catalyzed etherification of bio-glycerol and isobutylene over sulfonic mesostructured silicas. *Appl Catal A* 2008;346:44–51.
- [6] Bowman M, Hilligoss D, Rasmussen S, Thomas R. Biodiesel: a renewable and biodegradable fuel. *Hydrocarbon Process* 2006;85:103–6.
- [7] Smith C. Biodiesel revolution gathering momentum; 2004. <http://www.straight.com/print/3568> [accessed January 8, 2009].
- [8] Kenkel P, Holcomb R. Feasibility of on-farm or small scale oilseed processing and biodiesel. In: English BC, Menard J, Jensen K, editors. *Integration of agricultural and energy systems*. Atlanta, Georgia: Global Bioenergy Partnership; 2008.
- [9] Paliagro M, Rossi M. The future of glycerol: new uses of a versatile raw material. *RSC Green Chem* 2008;5:212–8.
- [10] Nilles D. Combating the glycerin glut. *Biodiesel Mag* 2006;6:5–6.
- [11] Kolmetz K, Ng WK, Faessler PW. Optimize process operation with new vacuum distillation methods. *Hydrocarbon Process* 2005;84:77–85.
- [12] da Silva GP, Mack M, Contiero J. Glycerol: a promising and abundant carbon source for industrial microbiology. *Biotechnol Adv* 2009;27:30–9.
- [13] Wang S, Guin JA, Xinhe B, Yide X. Synthesis of gasoline additives from methanol and olefins over sulfated silica. *Stud Surf Sci Catal* 2004;439–44.
- [14] Ribeiro NM, Pinto AC, Quintella CM. The role of additives for diesel and diesel blended (ethanol or biodiesel) fuels: a review. *Energy Fuels* 2007;21:2433–45.
- [15] <http://www.chevron.com/products/oronite/products/fuel-additives.html> [accessed January 8, 2009].
- [16] Rakopoulos CD, Rakopoulos DC, Hountalas DT, Giakoumis EG, Andritsakis EC. Performance and emissions of bus engine using blends of diesel fuel with biodiesel of sunflower or cottonseed oils derived from Greek feedstock. *Fuel* 2008;87:147–57.
- [17] Lin CY, Chen WC. Effects of potassium sulfide content in marine diesel fuel oil on emission characteristics of marine furnaces under varying humidity of inlet air. *Ocean Eng* 2006;33:1260–70.
- [18] Forester DR, Robert SDC, Manka JS, Malik BB. Jet fuel additive concentrate composition and fuel composition and methods thereof. US Patent WO2003106595; 2003.
- [19] Burtischer H, Matter U, Skillas G. The effect of fuel additives on diesel engine particulate emissions. *J Aerosol Sci* 1999;30:S851–2.
- [20] Jelles SJ, Krul RR, Makkee M, Moulijn JA. The influence of NOx on the oxidation of metal activated diesel soot. *Catal Today* 1999;53:623–30.
- [21] Yang HH, Lee WJ, Mi HH, Wong CH, Chen CB. PAH emissions influenced by Mn-based additive and turbocharging from a heavy-duty diesel engine. *Environ Int* 1998;24:389–403.
- [22] Gonzalez-Olmos R, Iglesias M. Thermodynamics and kinetics of fuel oxygenate adsorption into granular activated carbon. *J Chem Eng Data* 2008;53:2556–61.
- [23] Huang Z, Lu H, Jiang D. Performance and emissions of a compression ignition engine fueled with diesel/oxygenate blends for various fuel delivery advance angles. *Energy Fuels* 2005;19:403–10.
- [24] Marchetti AA, Knize MG, Chiarappa-Zucca ML, Pletcher RJ, Layton DW. Biodegradation of potential diesel oxygenate additives: dibutyl maleate (DBM), and tripropylene glycol methyl ether (TGME). *Chemosphere* 2003;52:861–8.
- [25] Nord KE, Haupt D. Reducing the emission of particles from a diesel engine by adding an oxygenate to the fuel. *Environ Sci Technol* 2005;39:6260–5.
- [26] Noureddini H. Production of oxygenated biodiesel fuel of low cloud point. US Patent 6015440-A; 2000.
- [27] Yu-hui G, Ben-xian S. QSAR Research of the activity of span surfactants as wax antisepting additives for diesel. *Energy Fuels* 2006;20:1579–83.
- [28] Suzuki K, Yuge K, Uchikawa K, Kakugawa K. Effect of fuel additives on reduction of smoke and particulate matter and stabilization of cycle-to-cycle variation. *J Jpn Pet Inst* 2005;48:229–36.
- [29] Suppes GJ, Goff M, Burkhart ML. Multifunctional diesel fuel additives from triglycerides. *Energy Fuels* 2000;15:151–7.
- [30] Zinenko SA, Egorov SA, Makarov AA. Miakron-2000 cetane-number-increasing additive for diesel fuels. *Chem Tech Fuel Oil* 2002;38:303–8.
- [31] http://en.wikipedia.org/wiki/Fuel_additive [accessed January 8, 2009].
- [32] Sood J, Rose G, Rahkamo R. Gasoline, the environment and economics. *Hydrocarbon Process* 1998;77:120C.
- [33] Satgé de Caro P, Mouloungui Z, Vaitilingom G, Berge JC. Interest of combining an additive with diesel-ethanol blends for use in diesel engines. *Fuel* 2001;80:565–74.
- [34] Demirbas A. Biofuels sources, biofuel policy, biofuel economy and global biofuel projections. *Energy Convers Manage* 2008;49:2106–16.
- [35] Wheals AE, Basso LC, Alves DMG, Amorim HV. Fuel ethanol after 25 years. *Trends Biotechnol* 1999;17:482–7.
- [36] Quintero JA, Montoya MI, Sánchez OJ, Giraldo OH, Cardona CA. Fuel ethanol production from sugarcane and corn: comparative analysis for a Colombian case. *Energy* 2008;33:385–99.
- [37] Prasad S, Singh A, Joshi HC. Ethanol as an alternative fuel from agricultural, industrial and urban residues. *Resour Conserv Recycl* 2007;50:1–39.
- [38] Patzek T, Anti SM, Campos R. Ethanol from corn: clean renewable fuel for the future, or drain on our resources and pockets? *Environ Dev Sust* 2005;7:319–36.
- [39] Kadam KL. Environmental benefits on a life cycle basis of using bagasse-derived ethanol as a gasoline oxygenate in India. *Energy Policy* 2002;30:371–84.
- [40] Hu Z, Tan P, Pu G. Multi-objective optimization of cassava-based fuel ethanol used as an alternative automotive fuel in Guangxi, China. *Appl Energy* 2006;83:819–40.
- [41] He BQ, Jian-Xin W, Hao JM, Yan XG, Xiao JH. A study on emission characteristics of an EFI engine with ethanol blended gasoline fuels. *Atmos Environ* 2003;37:949–57.
- [42] Pouloupoulos S, Philippopoulos C. Influence of MTBE addition into gasoline on automotive exhaust emissions. *Atmos Environ* 2000;34:4781–6.
- [43] Interagency assessment of oxygenated fuels. Washington, DC: Council NSaT; 1997.
- [44] Zervas E, Montagne X, Lahaye J. Emission of alcohols and carbonyl compounds from a spark ignition engine. Influence of fuel and air/fuel equivalence ratio. *Environ Sci Technol* 2002;36:2414–21.
- [45] Shi X, Yu Y, He H. Emission characteristics using methyl soyate-ethanol-diesel fuel blends on a diesel engine. *Fuel* 2005;84:1543–9.
- [46] Corro G, Ayala E. Bioethanol and diesel/bioethanol blends emissions abatement. *Fuel* 2008;87:3537–42.
- [47] Choi CY, Reitz RD. An experimental study on the effects of oxygenated fuel blends and multiple injection strategies on DI diesel engine emissions. *Fuel* 1999;78:1303–17.
- [48] Fernando S, Hanna M. Development of a novel biofuel blend using ethanolâ Biodieselâ diesel microemulsions: EB-diesel. *Energy Fuels* 2004;18:1695–703.
- [49] Franklin PM, Koshland CP, Lucas D, Sawyer RF. Clearing the air: using scientific information to regulate reformulated fuels. *Environ Sci Technol* 2000;34:3857–63.
- [50] Romanow. Perception becomes reality. *Hydrocarbon Process* 1999;78:13.
- [51] Oxyfuels information needs. Washington, DC: Agency USEP; 1996.
- [52] Achten C, Kolb A, Püttmann W. Methyl tert-butyl ether (MTBE) in urban and rural precipitation in Germany. *Atmos Environ* 2001;35:6337–65.
- [53] Arp HPH, Fenner K, Schmidt TC. Predicting methyl tert-butyl ether, tert-butyl formate, and tert-butyl alcohol levels in the environment using the fugacity approach. *Environ Sci Technol* 2005;39:3237–44.

- [54] Arp HPH, Schmidt TC. Air and water transfer of MTBE, its degradation products, and alternative fuel oxygenates: the role of temperature. *Environ Sci Technol* 2004;38:5405–12.
- [55] Gonzalez-Olmos R, Iglesias M. Study of fuel oxygenates solubility in aqueous media as a function of temperature and tert-butyl alcohol concentration. *Chemosphere* 2008;71:2098–105.
- [56] Kolb A, Püttmann W. Comparison of MTBE concentrations in groundwater of urban and nonurban areas in Germany. *Water Res* 2006;40:3551–8.
- [57] Rosell M, Lacorte S, Barceló D. Analysis, occurrence and fate of MTBE in the aquatic environment over the past decade. *Trends Anal Chem* 2006;25:1016–29.
- [58] Rosell M, Lacorte S, Barceló D. Simultaneous determination of methyl tert-butyl ether, its degradation products and other gasoline additives in soil samples by closed-system purge-and-trap gas chromatography–mass spectrometry. *J Chromatogr A* 2006;1132:28–38.
- [59] Schmidt TC, Haderlein SB, Pfister R, Forster R. Occurrence and fate modeling of MTBE and BTEX compounds in a Swiss Lake used as drinking water supply. *Water Res* 2004;38:1520–9.
- [60] Werner I, Koger CS, Deanovic LA, Hinton DE. Toxicity of methyl-tert-butyl ether to freshwater organisms. *Environ Pollut* 2001;111:83–8.
- [61] Bradley PM, Landmeyer JE, Chapelle FH. Widespread potential for microbial MTBE degradation in surface-water sediments. *Environ Sci Technol* 2001;35:658662.
- [62] Deeb RA, Hu HY, Hanson JR, Scow KM, Alvarez-Cohen L. Substrate interactions in BTEX and MTBE mixtures by an MTBE-degrading isolate. *Environ Sci Technol* 2000;35:312–7.
- [63] Purswani J, Pozo C, Rodriguez-Diaz M, Gonzalez-Lopez J. Selection and identification of bacterial strains with methyl-tert-butyl ether, ethyl-tert-butyl ether, and tert-amyl methyl ether degrading capacities. *Environ Toxicol Chem* 2008;27:2296–303.
- [64] Chang PBL, Young TM. Kinetics of methyl tert-butyl ether degradation and by-product formation during UV/hydrogen peroxide water treatment. *Water Res* 2000;34:2233–40.
- [65] Hong S, Zhang H, Duttweiler CM, Lemley AT. Degradation of methyl tertiary-butyl ether (MTBE) by anodic Fenton treatment. *J Hazard Mater* 2007;144:29–40.
- [66] Salari D, Daneshvar N, Aghazadeh F, Khataee AR. Application of artificial neural networks for modeling of the treatment of wastewater contaminated with methyl tert-butyl ether (MTBE) by UV/H₂O₂ process. *J Hazard Mater* 2005;125:205–10.
- [67] Sutherland J, Adams C, Kekobad J. Treatability of alternative fuel oxygenates using advanced oxidation, air stripping, and carbon adsorption. *J Environ Eng ASCE* 2005;131:623–31.
- [68] Lee S-W, Satio Y. Experimental investigation of the characteristics of an NOx reduction system for a dimethyl ether engine. *Proc Inst Mech Eng D J Aut Eng* 2005;219:89–96.
- [69] Ntziachristos L, Samaras Z, Pistikopoulos P, Kyriakis N. Statistical analysis of diesel fuel effects on particle number and mass emissions. *Environ Sci Technol* 2000;34:5106–14.
- [70] Yanfeng G, Shenghua L, Hejun G, Tiegang H, Longbao Z. A new diesel oxygenate additive and its effects on engine combustion and emissions. *Appl Therm Eng* 2007;27:202–7.
- [71] Ying W, Longbao Z, Hewu W. Diesel emission improvements by the use of oxygenated DME/diesel blend fuels. *Atmos Environ* 2006;40:2313–20.
- [72] Perry RH, Green DW, Maloney JOH. Perry's chemical engineers' handbook, 7th ed., McGraw-Hill; 1997.
- [73] Brady JE. General chemistry principal and structure, 5th ed., 2007.
- [74] Gesslein BW. Humectants in personal care formulation: a practical guide. In: Schueller R, Romanowski P, editors. Conditioning agents for hair and skin. Marcel Dekker, Inc.; 1999. p. 95–6.
- [75] Duane TJ, Katherine AT. The glycerin glut: options for the value-added conversion of crude glycerol resulting from biodiesel production. *Environ Prog* 2007;26:338–48.
- [76] Yang G, Tian J, Li J. Fermentation of 1,3-propanediol by a lactate deficient mutant of *Klebsiella oxytoca* under microaerobic conditions. *Appl Microbiol Biotechnol* 2007;73:1017–24.
- [77] Gatgens C, Degner U, Bringer-Meyer S, Herrmann U. Biotransformation of glycerol to dihydroxyacetone by recombinant *Gluconobacter oxydans* DSM 2343. *Appl Microbiol Biot* 2007;76:553–9.
- [78] Song H, Lee SY. Production of succinic acid by bacterial fermentation. *Enzyme Microb Technol* 2006;39:352–61.
- [79] Imandi SB, Bandaru VR, Somalanka SR, Garapati HR. Optimization of medium constituents for the production of citric acid from byproduct glycerol using Doehlert experimental design. *Enzyme Microb Technol* 2007;40:1367–72.
- [80] Solaiman DK, Ashby RD, Foglia TA, Marmer WN. Conversion of agricultural feedstock and coproducts into poly(hydroxyalkanoates). *Appl Microbiol Biot* 2006;71:783–9.
- [81] Nouredini H. System and process for producing biodiesel fuel with reduced viscosity and a cloud point below thirty-two (32) degrees fahrenheit. US Patent 6,174,501; 2001.
- [82] Gupta VP. Glycerine ditertiary butyl ether preparation. US Patent 5,476,971; 1995.
- [83] Bradin DS. Biodiesel fuel. US Patent 5,578,090; 1996.
- [84] Jalinski TJ. Bio-diesel fuel comprises fatty acid ester, and glycerol derived acetal ester or ketal ester miscible in fatty acid ester, as combustible component. US Patent WO2006084048-A1; 2006.
- [85] Delgado PJ. Procedure to obtain biodiesel fuel with improves properties at low temperature. EP Patent 1,331,260 A2; 2003.
- [86] Ferreira P, Fonseca IM, Ramos AM, Vital J, Castanheiro JE. Esterification of glycerol with acetic acid over dodecamolybdophosphoric acid engaged in USY zeolite. *Catal Commun* 2009;10:481–4.
- [87] Gonçalves VLC, Pinto BP, Silva JC, Mota CJA. Acetylation of glycerol catalyzed by different solid acids. *Catal Today* 2008;133–135:673–7.
- [88] Luque R, Budarin V, Clark JH, Macquarrie DJ. Glycerol transformations on polysaccharide derived mesoporous materials. *Appl Catal B* 2008;82:157–62.
- [89] Melero JA, van Grieken R, Morales G, Paniagua M. Acidic mesoporous silica for the acetylation of glycerol: synthesis of bioadditives to petrol fuel. *Energy Fuels* 2007;21:1782–91.
- [90] Delfort B, Durand I, Jaeger A. Diesel fuel compositions with reduced particulate emission, containing carbonate esters of glycerol acetal derivatives. EP 1,321,503-A; 2001.
- [91] Delfort B, Durand I, Jaeger A. Diesel fuel compositions containing glycerol acetals for particulate emission reduction. US Patent 6,890,364, 2005.
- [92] Delfort B, Durand I, Jaeger A. Fuel additive of an ether and group 2a metal salt. EP Patent 1,321,502-A; 2001.
- [93] Kesling S, Karas LJ, Liotta FJ. Diesel fuel. US Patent 5,308,365; 1994.
- [94] Margolese D, Melero JA, Christiansen SC, Chmelka BF, Stucky GD. Direct syntheses of ordered SBA-15 mesoporous silica containing sulfonic acid groups. *Chem Mater* 2000;12:2448–59.
- [95] Wessendorf R. Derivatives of glycerol as components of fuels. *Petrochemie* 1995;48:138–43.
- [96] Weirauch W. HPImpact. *Hydrocarbon Process* 2002;81:21.
- [97] Bradin D, Grune GL, Trivette M. Alternative fuel composition for use in gasoline, diesel, marine diesel, jet and flexible fuel engines, comprises fuel/alcohol blend and glycerol ether or mixture of glycerol ethers. US Patent WO2007061903-A1; 2007.
- [98] Hazel CJ, Williamson IV. Fuel composition. US Patent 607,445; 2002.
- [99] Bradin DS. Fuel additive composition useful in bio-diesel fuels comprises fatty acid alkyl ester(s), glyceryl ether(s) and tri-glyceride(s). US Patent 5,578,090-A; 1996.
- [100] Klepáčová K, Mravec D, Kaszonyi A, Bajus M. Etherification of glycerol and ethylene glycol by isobutylene. *Appl Catal A* 2007;328:1–13.
- [101] Praveen RM, Brammer SC, Nouredini H. Improved conversion of plant oils and animal fats into biodiesel and co-product. *Bioresour Technol* 1996;56:19–24.
- [102] Klepáčová K, Mravec D, Bajus M. tert-Butylation of glycerol catalysed by ion-exchange resins. *Appl Catal A* 2005;294:141–7.
- [103] Nouredini H, Daily WR, Hunt BA. Production of ethers of glycerol from crude glycerol—the by-product of biodiesel production. *Chem Biomol Eng Res* 1998;13:121–9.
- [104] Karinen RS, Krause AOI. New biocomponents from glycerol. *Appl Catal A* 2006;306:128–33.
- [105] Garcia E, Laca M, Perez E, Garrido A, Peinado J. New class of acetal derived from glycerin as a biodiesel fuel component. *Energy Fuels* 2008;22:4274–80.
- [106] Agnieszka MR, Johannes DM, Bonny WM, Kuipers BH, Erné BM. Glycerol etherification over highly active CaO-based materials: new mechanistic aspects and related colloidal particle formation. *Chem Eur J* 2008;14:2016–24.
- [107] Clacens JM, Pouilloux Y, Barrault J. Selective etherification of glycerol to polyglycerols over impregnated basic MCM-41 type mesoporous catalysts. *Appl Catal A* 2002;227:181–90.
- [108] Clacens JM, Pouilloux Y, Barrault J. Synthesis and modification of basic mesoporous materials for the selective etherification of glycerol. *Stud Surf Sci Catal* 2000;687–95.
- [109] Richter M, Krisnandi YK, Eckelt R, Martin A. Homogeneously catalyzed batch reactor glycerol etherification by CsHCO₃. *Catal Commun* 2008;9:2112–6.
- [110] Cardona C, Posada J, Montoya M. Use of glycerol from biodiesel production: conversion to added value products. In: Proceedings of European congress of chemical engineering (ECCE-6); 2007.
- [111] Wang K, Hawley MC, DeAthos SJ. Conversion of glycerol to 1,3-propanediol via selective dehydroxylation. *Ind Eng Chem Res* 2003;42:2913–23.
- [112] Chi Z, Pyle D, Wen Z, Frear C, Chen S. A laboratory study of producing docosahexaenoic acid from biodiesel-waste glycerol by microalgal fermentation. *Process Biochem* 2007;42:1537–45.
- [113] Aresta M, Dibenedetto A, Nocito F, Pastore C. A study on the carboxylation of glycerol to glycerol carbonate with carbon dioxide: the role of the catalyst, solvent and reaction conditions. *J Mol Catal A* 2006;257:149–53.
- [114] Lee SH, Park DR, Kim H. Direct preparation of dichloropropanol (DCP) from glycerol using heteropolyacid (HPA) catalysts: a catalyst screen study. *Catal Commun* 2008;9:1920–3.
- [115] Ullmann's encyclopedia of industrial chemistry, 6th ed., Weinheim: Wiley-VCH; 2002.
- [116] Biebl H. Fermentation of glycerol by *Clostridium pasteurianum*—batch and continuous culture studies. *J Ind Microbiol Biotechnol* 2001;27:18–26.
- [117] Huber GW, Shabaker JW, Dumesic JA. Raney Ni–Sn catalyst for H₂ production from biomass-derived hydrocarbons. *Science* 2003;300:2075–7.
- [118] Adhikari S, Fernando SD, Haryanto A. Hydrogen production from glycerol by steam reforming over nickel catalysts. *Renew Energy* 2008;33:1097–100.
- [119] Wen G, Xu Y, Ma H, Xu Z, Tian Z. Production of hydrogen by aqueous-phase reforming of glycerol. *Int J Hydrogen Energy* 2008;33:6657–66.
- [120] Zhang B, Tang X, Li Y, Xu Y, Shen W. Hydrogen production from steam reforming of ethanol and glycerol over ceria-supported metal catalysts. *Int J Hydrogen Energy* 2007;32:2367–73.

- [121] Corma A, Huber GW, Sauvanaud L, O'Connor P. Biomass to chemicals: catalytic conversion of glycerol/water mixtures into acrolein, reaction network. *J Catal* 2008;257:163–71.
- [122] Watanabe M, Iida T, Aizawa Y, Aida TM, Inomata H. Acrolein synthesis from glycerol in hot-compressed water. *Bioresour Technol* 2007;98:1285–90.
- [123] Zhou C-J, Huang C-J, Zhang W-G, Zhai H-S, Wu H-L, Chao Z-S. Synthesis of micro- and mesoporous ZSM-5 composites and their catalytic application in glycerol dehydration to acrolein. *Stud Surf Sci Catal* 2007;527–30.
- [124] Tsukuda E, Sato S, Takahashi R, Sodesawa T. Production of acrolein from glycerol over silica-supported heteropoly acids. *Catal Commun* 2007;8:1349–53.
- [125] Ning L, Ding Y, Chen W, Gong L, Lin R, Lu Y, et al. Glycerol dehydration to acrolein over activated carbon-supported silicotungstic acids. *Chin J Catal* 2008;29:212–4.
- [126] Lee PC, Lee WG, Lee SY, Chang HN. Succinic acid production with reduced by-product formation in the fermentation of *Anaerobiospirillum succiniciproducens* using glycerol as a carbon source. *Biotechnol Bioeng* 2001;72:41–8.
- [127] Pollington SD, Enache DI, Landon P, Meenakshisundaram S, Dimitratos N, Wagland A, et al. Enhanced selective glycerol oxidation in multiphase structured reactors. *Catal Today* 2009;145:169–75.
- [128] Demirel-Gülen S, Lucas M, Claus P. Liquid phase oxidation of glycerol over carbon supported gold catalysts. *Catal Today* 2005;102–103:166–72.
- [129] Leonhard Ohrem H, Voß H. Process model of the oxidation of glycerol with *gluconobacter oxydans*. *Process Biochem* 1996;31:295–301.
- [130] Ciriminna R, Palmisano G, Pina CD, Rossi M, Pagliaro M. One-pot electrocatalytic oxidation of glycerol to DHA. *Tetrahedron Lett* 2006;47:6993–5.
- [131] Jamróz ME, Jarosz M, Witowska-Jarosz J, Bednarek E, Tecza W, Jamroz MH, et al. Mono-, di-, and tri-tert-butyl ethers of glycerol: a molecular spectroscopic study. *Spectrochim Acta A Mol Biomol Spectrosc* 2007;67:980–8.
- [132] Dmytryshyn SL, Dalai AK, Chaudhari ST, Mishra HK, Reaney MJ. Synthesis and characterization of vegetable oil derived esters: evaluation for their diesel additive properties. *Bioresour Technol* 2004;92:55–64.